A Preliminary Investigation Into the Presence of Agricultural Pesticides in the La Salle and Assiniboine Rivers, Manitoba, Canada

Water Standards and Studies, Report #84-5

Manitoba
Environment and
Workplace Safety
and Health

A Preliminary Investigation into the Presence of Agricultural Pesticides in the La Salle and Assiniboine Rivers, Manitoba, Canada

D. A. Williamson
Water Standards and Studies Section
Environmental Management Services Branch
Department of Environment and
Workplace Safety and Health.

Water Standards and Studies Report #84-5

Please Note: Mention of product names within this report should not be construed as meaning approval, endorsement or recommendation of such products by the Manitoba Department of Environment and Workplace Safety and Health.

EXECUTIVE SUMMARY

The La Salle River, Manitoba, Canada, is being considered as a source for municipal domestic water supply. One such project, entitled the "Elie Aquifer Enhancement Project" proposed to divert surface water from the La Salle River into a near-surface groundwater aquifer. Groundwater from this aquifer provides the Town of Elie with domestic water supply. However in recent years, this aquifer has become increasingly saline due to salt-water intrusion from lower aquifers. It was expected that enhancement of this near-surface aquifer with La Salle River water would alleviate the taste concerns resulting from this natural increase in dissolved mineral content. Because of the extensive agricultural land-use activities within the La Salle River watershed, delineation of pesticide concentrations within the La Salle River was necessary prior to determining the suitability of such water for this groundwater recharge project.

Water samples were collected from the La Salle and Assiniboine Rivers during 1983/1984 and were analyzed for twenty-seven agricultural pesticides. The herbicides triallate, trifluralin, dicamba, MCPA, diclofop-methyl and 2,4-D plus the insecticide azinphos-methyl were detected in samples collected from the La Salle River. The herbicides triallate, trifluralin, dicamba and MCPA were detected in samples collected from the Assiniboine River. The mechanism of transport was not part of this investigation, but appeared related to snow-melt and rainfall runoff events.

Ambient concentrations of trifluralin, azinphos-methyl, dicamba, MCPA and 2,4-D did not exceed the available criteria derived for the protection of human health following long-term consumption. Further investigations, however, are required to determine the significance of the reported carcinogenic response exhibited by trifluralin towards one laboratory animal species tested.

The scientific information is too limited to determine the human health significance of the measured triallate concentrations in the La Salle and Assiniboine Rivers and the diclofop-methyl concentrations in the La Salle River.

It appeared that the measured concentrations of trifluralin, dicamba, MCPA, diclofop-methyl and 2,4-D in the La Salle River and trifluralin, dicamba and MCPA in the Assiniboine River should not pose a chronic threat to aquatic life. However, it appeared probable that azinphos-methyl concentrations in the La Salle River exceeded calculated tentative water quality objectives suitable for the long-term protection of aquatic life.

The scientific information is too limited to determine the significance of the measured concentrations of triallate towards aquatic life.

Williamson, D. A., 1984. A preliminary investigation into the presence of agricultural pesticides in the La Salle and Assiniboine Rivers, Manitoba, Canada. Environmental Management Services Branch, Manitoba Department of Environment and Workplace Safety and Health, Water Standards and Studies Report #84-5.

Abstract

Water samples were collected from the La Salle and Assiniboine Rivers during 1983/84 and were analyzed for twenty-seven agricultural pesticides. The herbicides triallate, trifluralin, dicamba, MCPA, diclofop-methyl and 2,4-D plus the insecticide azinphos-methyl were detected in samples collected from the La Salle River. The herbicides triallate, trifluralin, dicamba and MCPA were detected in samples collected from the Assiniboine River. The mechanism of transport was not part of this investigation, but appeared related to snow-melt and rainfall runoff events. Environmental fate and effect considerations are examined and comparisons are made to available criteria derived for the protection of drinking water and aquatic life and wildlife.

Table of Contents

	Page
Executive Summary	ii
Abstract	iv
Table of Contents	v
List of Figures	vi
List of Tables	vi
1. Introduction	1
1.1 Study Area	3
1.1.1 La Salle River Watershed	3
1.1.2 Assiniboine River Watershed	3
2. Methods	5
3. Results and Discussion	6
3.1 Triallate	6
3.2 Trifluralin	9
3.3 Azinphos-methyl	15
3.4 Dicamba	18
3.5 MCPA	21
3.6 Diclofop-methyl	24
3.7 2,4-D	26
4. Conclusions	29
5. References	33
6. Acknowledgements	37

List of Figures

Page

Figure 1: Map outlining the study area and the sampling sites..... 4

List of Tables

Page

Table 1: Pesticides analyzed in surface water samples collected from the La Salle and Assiniboine Rivers, with associated detection limits and recovery efficiencies. 2

Table 2: Concentrations (µg/L) of triallate in surface waters within the study area..... 7

Table 3: Concentrations (µg/L) of trifluralin in surface waters within the study area..... 10

Table 4: Concentrations (µg/L) of azinphos-methyl in surface waters within the study area..... 16

Table 5: Concentrations (µg/L) of dicamba in surface waters within the study area..... 19

Table 6: Concentrations (µg/L) of MCPA in surface waters within the study area..... 22

Table 7: Concentrations (µg/L) of diclofop-methyl in surface waters within the study area..... 25

Table 8: Concentrations (µg/L) of 2,4-D in surface waters within the study area..... 27

Table 9: Summary of the pesticide results, with available criteria for the protection of drinking water and criteria for the protection of aquatic life..... 32

1. Introduction

Attempts to maximize agricultural productivity has resulted in the need to more efficiently eliminate weed competition and to reduce crop damage due to ingestion by insect and decay by microbiological pests. Thus, there has been a trend in recent years towards an increase in the quantity of pesticides used, and in the number of available formulations.

Pesticide migration from the application site may occur through internal soil drainage, storm runoff or snow-melt events. Pesticide losses to surface waters may also occur due to spray drift, direct discharge, such as losses during filling and rinsing operations, or direct application.

Transport mechanisms are complex and include factors such as water solubility, volatility from water and soil and adsorption to soil organic matter. The environmental fate is also dependent upon numerous complex interactions such as the effects of temperature, rate of pesticide intake, bioadsorption and bioabsorption. Other factors such as the partial coefficient between n - octonal and water, soil and water, and water and air are important regarding the bioaccumulation potential (Haque and Freed, 1975).

Agricultural pesticides have been detected in surface waters draining farmlands by numerous researchers, including Miles et al (1971), Miles and Harris (1973), Frank et al (1974), Frank and Sirons (1979), Roberts et al (1979), Frank et al (1980), Environment Canada (1980), Frank et al (1981), Frank et al (1982), and Environment Canada (1982). Infiltration of contaminated surface waters into underlying aquifers has also resulted in the transport of agricultural pesticide residues into groundwaters (Zaki et al, 1982) (O'Brien and Fisher, 1983).

This present investigation was conducted in order to determine the nature and extent of contamination of the La Salle and Assiniboine Rivers by agricultural pesticides in the vicinity of Elie, Manitoba.

Analyses were conducted for 27 pesticides. This included 7 chlorinated phenoxy compounds, 14 organochlorines, 4 organophosphates and 2 organonitrogen or miscellaneous pesticides (Table 1).

Table 1: Pesticides analyzed in surface water samples collected from the La Salle and Assiniboine Rivers, with associated detection limits and recovery efficiencies.

Common Name	Detection Limit (µg/L)	Recovery Efficiency (%)
Chlorinated Phenoxy Pesticides		
2,4-D	0.007	95 ± 14
Silvex	0.002	76 ± 11
2,4,5-T	0.003	86 ± 11
2,4-DB	0.022	64 ± 22
MCPA	0.5	82 ± 19
Dicamba	0.5	81 ± 46
Diclofop-methyl	0.5	96 ± 12
Organochlorine Pesticides		
Lindane	0.001	85 ± 6.2
Aldrin	0.002	93 ± 5.7
Dieldrin	0.004	98 ± 5.7
Endrin	0.008	99 ± 4.3
Cis-Chlordane	0.004	97 ± 5.0
Trans-Chlordane	0.003	99 ± 4.4
o, p' - DDE	0.004	97 ± 5.0
p, p' - DDE	0.003	98 ± 6.0
o, p' - DDD	0.007	97 ± 3.3
p, p' - DDD	0.009	95 ± 4.3
o, p' - DDT	0.007	98 ± 4.0
p, p' - DDT	0.008	107 ± 8.0
Methoxychlor	0.030	93 ± 10.8
Triallate	0.05	96 ± 15
Organophosphorus Pesticides		
Methyl-parathion	0.047	96 ± 4.2
Ethyl - parathion	0.054	95 ± 7.9
Azinphos-methyl	0.5	102 ± 4
Diazinon	0.018	89 ± 9
Organonitrogen and Miscellaneous Pesticides		
Trifluralin	0.05	99 ± 9
Bromoxynil	0.5	96 ± 3

1.1 Study Area

1.1.1 La Salle River Watershed

The La Salle River watershed is approximately 2147 km^2 and is located entirely within south-central Manitoba (Fedoruk, 1970). Surface deposits are mainly clay and silt with some marsh and rock out-crops. Soils are generaly of the black-fine textured type.

The area is intensively farmed and produces cereal, oil seed, corn, potatoe and vegetable crops. Livestock production is also significant within this watershed.

Natural flow regimes on the La Salle River are influenced by numerous dams located at various points along the entire length of the stream. Historical mean flows are 0.302 m^3/s with the highest flows predictably being recorded during spring runoff. Historical mean flows during April and May are 1.34 m^3/s and 0.971 m^3/s, respectively (Water Survey of Canada, 1983).

Exchange occurs between surface and groundwaters in some reaches of the La Salle River . Intrusion of saline groundwater during low flow periods has resulted in surface water conductivities ranging to 11000 µS/cm (Williamson, 1982).

The sampling sites on the La Salle River (Figure 1) monitored an effective drainage area of approximately 197.9 km^2 (Mowchenko and Meid, 1983). This area excludes marshes, sloughs and other natural storage areas that would not contribute runoff during "average" years.

1.1.2 Assiniboine River Watershed

The Assiniboine River watershed is approximately 47240.47 km^2, of which 24184.8 km^2 is within Manitoba. Soils within this area are variable. Agricultural land use activities in close proximity to the Assiniboine River include pastoral, forage, field crop and intensive vegetable crop production.

Historical annual mean flows in the Assiniboine River near the study area are 54.0 m^3/s. Historical mean monthly flows range from 168 m^3/s to 13.8 m^3/s for the months of May and February, respectively (Water Survey of Canada, 1983).

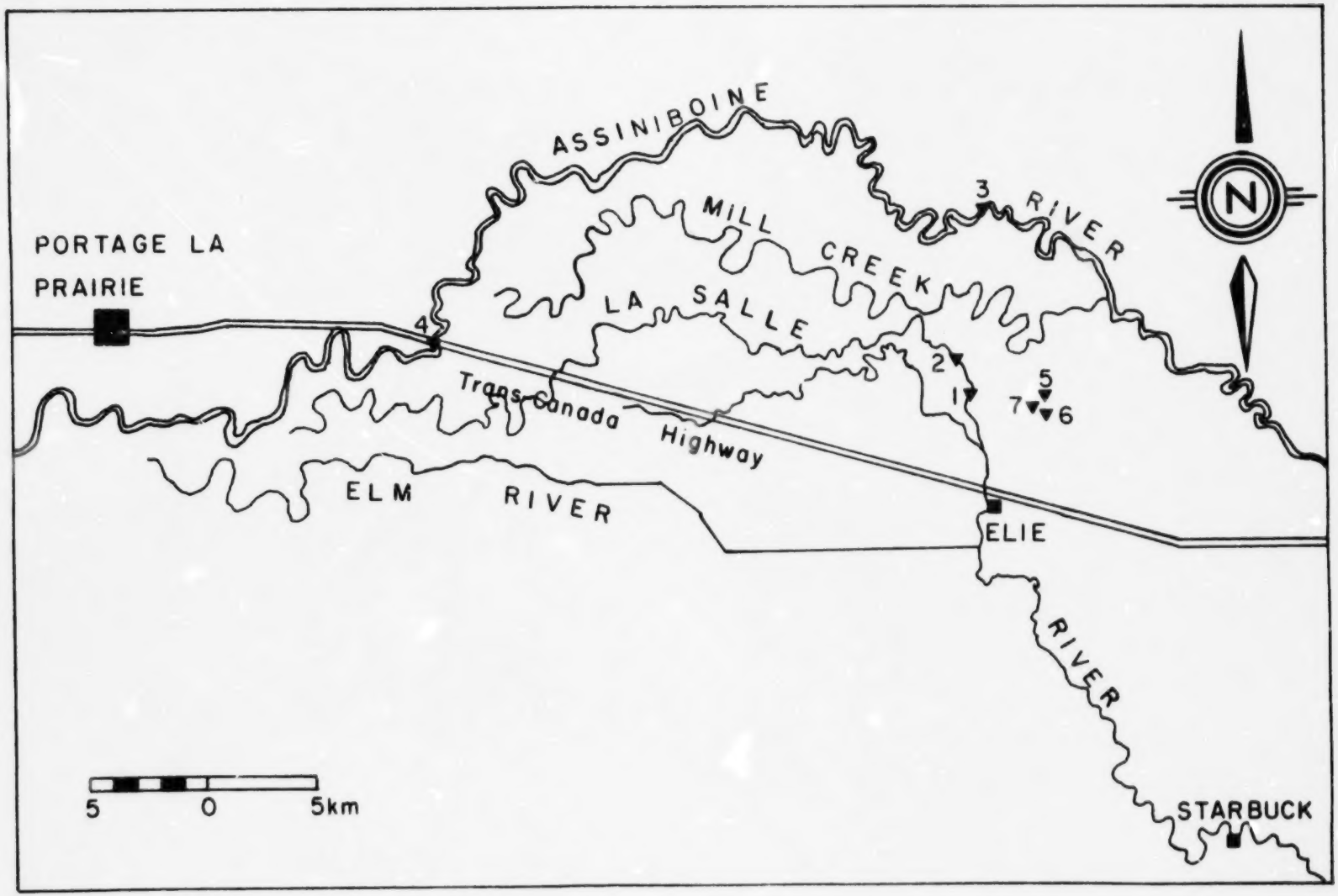

Figure 1: Map outlining the study area and the sampling sites.

The sampling sites on the Assiniboine River (Figure 1) monitored an effective drainage area of approximately 57752.6 km^2. The sampling sites were located downstream of the confluence of the Assiniboine and Souris Rivers, hence, drainage from the Souris River watershed would also have been included.

2. Methods

A survey of seven landowners in the Elie area was conducted in order to identify pesticide use patterns within the study area. The survey area encompassed approximately 10.7 square kilometers. The products Hoegrass (diclofop-methyl), Torch (bromoxynil), Avenge (difenzoquat), Buctril M (bromoxynil plus MCPA), MCPA, Guthion (azinphos-methyl), Avadex BW (triallate), Treflan (trifluralin), Pardner (bromoxynil) and Banvel M (dicamba plus MCPA) were used to control pests in wheat, barley, rapeseed, canary seed, peas and flax.

A total of twenty-seven water samples were collected for pesticide analyses from two sites (Figure 1) on the La Salle River on 16 occasions. Three additional samples were collected during April, 1983 for the analyses of all pesticides excepting triallate, trifluralin, azinphos-methyl, dicamba, MCPA, bromoxynil and diclofop-methyl. The sampling interval was clustered during April, 1983 in order to coincide with snow-melt water runoff. Samples were then collected at monthly intervals from May, 1983 to March, 1984, inclusive. Samples were not collected during August, 1983.

A total of fifteen samples were collected from two sites on the Assiniboine River on 10 occasions. Sampling was initiated in May, 1983 and continued at monthly intervals through March, 1984. Samples were not collected during August, 1983.

Additionally, single samples were collected on one occasion from three small surface water pools within the study area.

Pesticide samples were collected in acetone/hexane pre-washed/rinsed glass containers. Samples collected for the analyses of triallate, trifluralin, azinphos-methyl, dicamba, MCPA, bromoxynil and diclofop-methyl were acidified with phosphoric acid.

Samples were chilled to 4°C, then shipped via air freight to Enviro-Test Laboratories, Edmonton, Alberta for analyses. Samples for the remaining pesticides were immediately delivered to the W. M. Ward Technical Services Laboratory, Winnipeg, Manitoba, for analyses.

Laboratory methodology was dependent upon the specific pesticide or pesticide group. Generally, however, a one litre sample of water was extracted with 15% dichloromethane in hexane using separatory funnel techniques. If required, the organic extract was cleaned with a Florisil column, then concentrated. The sample was then identified, confirmed and quantified by Gas Liquid Chromatography, using electron capture ^{63}Ni or nitrogen/phosphorus detectors.

Analyses for triallate, trifluralin, azinphos-methyl, dicamba, MCPA, bromoxynil and diclofop-methyl were confirmed utilizing a Gas Chromotography/Mass Spectrometry system.

Following confirmational analyses through mass spectra comparison, several pesticide residue concentrations were reported as "trace", and in some cases, were approximately quantified, even though the concentrations were below the specific methods detection limits.

3. Results and Discussion

Although numerous pesticides were included in the sample analyses, residues of only triallate, trifluralin, azinphos-methyl, dicamba, MCPA, diclofop-methyl and 2,4-D were detected. The results for these pesticides will be discussed individually in the following sections.

3.1 Triallate

Triallate, namely S-(2,3,3-Trichloroallyl) diisopropylthiocarbamate, is the active ingredient contained in the herbicide Avadex BW. This pesticide is applied either as a granular or liquid compound and is incorporated into the top soil horizon. Avadex BW is used for the pre-emergence control of wildoats in a variety of cereal, oil seed and forage crops (Manitoba Agriculture, 1984b).

Table 2: Concentrations (µg/L) of triallate in surface waters within the study area.

	La Salle R. #1	La Salle R. #2	Assiniboine R. #3	Assiniboine R. #4	Surface Runoff #5	Surface Runoff #6	Surface Runoff #7
April 11, 1983	0.1	0.15					
April 13, 1983	0.07	0.1			Trace		
April 18, 1983	0.08	0.05					
April 20, 1983	0.08	0.08					
April 25, 1983	0.05	0.07					
April 27, 1983	0.06	0.08					
May 2, 1983	Trace[1,2]	0.06[2]	Trace[2]				
June 1, 1983						0.05	ND
June 14, 1983	Trace	Trace (0.03)	ND[5]				
July 13, 1983	Trace (0.02)	Trace (0.03)	Trace (0.04)				
September 12, 1983	0.05	Trace (0.04)	ND				
October 13, 1983	Trace (0.02)	Trace (0.02)	ND				
November 8, 1983	Trace (0.03)		Trace (0.03)	Trace (0.02)			
December 5, 1983	Trace (0.03)[3]		Trace (0.01)	Trace (0.01)			
January 5, 1984	Trace (0.03)		ND	Trace (0.01)			
February 21, 1984	Trace (0.04)		ND	ND			
March 26, 1984	Trace (0.03)[4]		ND	ND			

1. Detected by Gas Chromotography and confirmed by Mass Spectrometry. Concentrations have been quantified in some cases. However, these values may only be approximate since they are below the methods detection limits.

2. Analyses were performed on a decanted sample due to the formation of a surface layer of an apparent hydrocarbon.

3. Samples were filtered through Whatman #4 qualitative paper, prior to extraction. This filtration removed 98% of the 20-25 µm size particles.

4. Samples may have contained a large proportion of snow-melt water.

5. ND = Not Detected.

Triallate was detected in all samples collected from the La Salle River. Concentrations ranged from trace to 0.15 µg/L (Table 2).

Concentrations of triallate in the La Salle River were linearly correlated with flow (r^2 = .713; flow (m^3/s) = - 1.38 + 37.2 (µg/L triallate); $\rho \neq 0$, α = .05). This positive linear correlation appeared to indicate that the method of transport was by surface runoff as opposed to other migration pathways, such as internal soil drainage, direct contamination through spray drift, or losses from equipment during filling or rinsing operations.

Menzie (1974), following a review of the available information, concluded that degradation of triallate in soils is not rapid. Fifty percent of the triallate applied to moist Regina heavy clay and Weyburn loam remained after 8 to 11 weeks at 25°C. Fully 100% of the applied triallate was recovered from sterile soils. Further, after approximately 5 months, 16-27% of the applied triallate was recovered from the top 5 cm of soil. The environmental significance of this phenomenon is two fold. Firstly, similar degradation rates may occur in surface waters, resulting in the persistence of triallate for a long period of time after contamination. Secondly, following application to agricultural soils, triallate remains available for transport to surface or groundwaters for a considerable period of time.

While the limited data base is not conclusive, it would appear that triallate was present as dissolved residues. One sample, collected in December, 1983, was filtered through Whatman #4 qualitative paper prior to pesticide extraction. This filtration process removed 98% of the 20-25 µm size particles. Traces of triallate were detected and were not appreciably different from residues in samples collected during similar flow regimes.

Triallate was detected in 46% of the samples collected from the Assiniboine River. Concentrations, although below the detection limit of the method, were approximately quantified to range from trace to 0.04 µg/L.

A pattern of contamination in the Assiniboine River was not evident. Although speculative, triallate concentrations detected during November, 1983, December, 1983 and January, 1984 may have resulted from triallate migration during precipitation events subsequent to autumn application. Environment Canada (pers. comm.) recorded 9.6 mm of rainfall in the area for the period between sample collections in October, 1983 and November, 1983. Triallate was not detected in previous samples collected from the Assiniboine River during September and October, 1983.

Three samples were collected from ponded waters resulting from local surface runoff. Triallate was confirmed in two samples, with concentrations reported as trace and 0.05 µg/L.

The acute oral triallate LD_{50} for rats is reported to range from 1675 to 2165 mg/kg (Farm Chemicals, 1982.). Scientific drinking water criteria information is too limited to determine the significance of the observed triallate concentrations to human health. Further, scientific studies have not been undertaken to determine the significance of these concentrations with regard to aquatic life.

3.2 Trifluralin

Trifluralin, or α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-ρ-toluidine, is the active ingredient within the products Treflan EC, Treflan QR5, plus others. These products are used for the pre-emergence control of various weeds within a wide range of crops. For example, weeds such as barnyard grass, green foxtail, yellow foxtail, wildoats, wild buckwheat, plus others can be controlled within crops of barley, wheat, flax, mustard, rapeseed, soybeans, sunflowers, field beans, fababeans, lentils and peas (Manitoba Agriculture, 1984b).

Table 3: Concentrations (µg/L) of trifluralin in surface waters within the study area.

	La Salle R. #1	La Salle R. #2	Assiniboine R. #3	Assiniboine R. #4	Surface Runoff #5	Surface Runoff #6	Surface Runoff #7
April 11, 1983	Trace (0.03)[1]	0.05			Trace		
April 13, 1983	Trace	Trace					
April 18, 1983	0.16	Trace					
April 20, 1983	Trace	Trace					
April 25, 1983	Trace	Trace					
April 27, 1983	Trace	Trace					
May 2, 1983	ND[2,5]	Trace[2]	ND[2]				
June 1, 1983						Trace	ND
June 14, 1983	ND	ND	ND				
July 13, 1983	ND	ND	ND				
September 12, 1983	0.06	ND	ND				
October 13, 1983	Trace (0.01)	Trace (0.01)	ND				
November 8, 1983	0.24		0.1	Trace			
December 5, 1983	Trace[3]		Trace (0.01)	Trace (0.02)			
January 5, 1984	Trace (0.01)		ND	ND			
February 21, 1984	ND		ND	ND			
March 26, 1984	ND[4]		ND	ND			

1. Detected by Gas Chromotography and confirmed by Mass Spectrometry. Concentrations have been quantified in some cases. However, these values may only be approximate since they are below the methods detection limits.

2. Analyses were performed on a decanted sample due to the formation of a surface layer of an apparent hydrocarbon.

3. Samples were filtered through Whatman #4 qualitative paper, prior to extraction. This filtration removed 98% of the 20-25 µm size particles.

4. Samples may have contained a large proportion of snow-melt water.

5. ND = Not Detected.

Trifluralin was detected in 70% of samples collected from two sites on the La Salle River (Table 3). Concentrations ranged from trace to 0.24 µg/L. Trifluralin was also detected and confirmed in 27% of samples collected from two sites on the Assiniboine River. Concentrations ranged from trace to 0.1 µg/L.

The presence of trifluralin in both the La Salle and Assiniboine Rivers appeared to follow a biannual pattern. Concentrations were highest in both April and November, 1983. This biannual pattern of contamination may have resulted from trifluralin transport during spring snow-melt runoff and during autumn rainfall runoff events subsequent to respective autumn, 1982 and autumn, 1983 application. As previously discussed in Section 3.1.1, Environment Canada (pers. comm.) recorded 9.6 mm of rainfall in the area for the period between sample collection in October, 1983 and November, 1983. Trifluralin concentrations at one site on the La Salle River increased from trace (0.01 µg/L) to 0.24 µg/L during this period. Following peak elevations, trifluralin residues were then reduced to non-detectable concentrations. This degradation process appeared to occur at a slower rate in the autumn/winter period than in the spring. This may have been due to less than optimum conditions for microbial decomposition or photodegradation during the cooler autumn and winter season. Photochemical oxidation may have been reduced under ice and snow cover.

Trifluralin is stable when not exposed to light. Effective weed control may be achieved for four to six months following application. Additionally, sensitive crops may be damaged if planted within twenty-four months of autumn application (Manitoba Agriculture, 1984b).

Haque and Freed (1975) reported trifluralin to be moderately persistent in soils, with a half life of 1.5 to 6 months. Nash (1983) reported that volatilization, occurring at an exponential rate, accounted for loss of 60.3% of the applied trifluralin after 11 days. Since only 6.5% could be accounted for after soil analyses, it was speculated that photodegradation was responsible for losses of

vaporous trifluralin during application. Hence, trifluralin residues may be available for the potential transport to aquatic systems for a considerable period of time following application.

It was speculated that the measured trifluralin residues were present as dissolved substances. One sample, collected during December, 1983 and filtered through Whatman #4 qualitative paper, prior to extraction, contained trifluralin residues at trace levels.

Trifluralin was also detected and confirmed at trace concentrations in two single samples collected from ponded waters at three sites within the study area.

The National Academy of Sciences (1977) included a summary of trifluralin mammalian toxicity investigations. Following consideration of acute and chronic toxicity studies, the National Academy of Sciences (1977) recommended an Acceptable Daily Intake (ADI) for trifluralin of 0.1 mg/kg/day. The ADI is defined as the "maximum dose producing no observed adverse effect divided by the uncertainty factor". Assuming that 1% of this ADI could be ingested from drinking water, with the remaining 99% from other sources, such as food products, resulted in a drinking water criteria of 35.0 µg/L (this assumed that 2.0 L of water are consumed daily by a 70 kg person). The State of New York (1978) promulgated this concentration as a groundwater quality standard suitable for ensuring the protection of groundwater utilized for domestic consumption. However, assuming that 20% of this ADI could be ingested from drinking water, as opposed to 80% from other sources, the resultant drinking water criteria is 700.0 µg/L. This latter assumption is consistent with that utilized for the development of criteria for other pesticides by Health and Welfare Canada (1978).

It is conceivable, however, that the ADI recommended by the National Academy of Sciences (1977) would have been lower had more recent carcinogenic information on trifluralin been included. Griesemer and Cueto (1980) reported that trifluralin exhibits very strong evidence of carcinogenicity in one species of test animal, and none in a second species tested. However the National Academy of Sciences (1977) reported that no carcinogenic or tumorigenic effects had been documented.

Health and Welfare Canada has recognized the persistent nature of trifluralin and that possible adverse health effects may be elicited upon ingestion. Provisions of Division 15 of the Federal Food and Drug Regulations establish a maximum residue limit of 0.5 mg/kg trifluralin on carrots. Health and Welfare Canada utilized an acceptable daily intake of 0.01 mg/kg/day for the derivation of this maximum residue limitation (pers. comm., Dr. P. Toft). Assuming that 1% and 20% of this ADI could be ingested from drinking water, with the remainder available from other sources, resulted in a criteria of 3.5 µg/L and 70.0 µg/L, respectively.

It is unlikely that the lower ADI utilized by Health and Welfare Canada, when compared with that used by the National Academy of Sciences (1977) took into account the possible carcinogenicity of trifluralin that was reported by Griesemer and Cueto (1980). The lower ADI utilized by Health and Welfare Canada was based upon a review of literature in 1964 (Health and Welfare Canada, pers. comm.). Hence, the most recent carcinogenicity information would not have been included.

Based upon the available toxicity data, it appeared that aquatic organisms are considerably more sensitive to trifluralin than are land mammals. Macek et al (1969) reported the 96 hr TLm for rainbow trout (Salmo gairdneri) to range from 0.152 mg/L to 0.210 mg/L. The bluegill (Lepomis macrochirus) appeared slightly more sensitive with 96 hr TLm results ranging from 0.047 mg/L to 0.190 mg/L (Macek et al, 1969).

Johnson and Finley (1980) reported the 96 hr LC_{50} for trifluralin for several aquatic species. The acute toxicity for rainbow trout and bluegill were 0.041 mg/L and 0.105 mg/L, respectively.

Aquatic invertebrates apparently are more tolerant to trifluralin than are fish species. Acute toxicities, as demonstrated by 48 hr LC_{50} tests, were 0.193 mg/L for Daphnia magna (Macek et al, 1976), 5.6 mg/L for the scud Gammarus lacustris (Sanders, 1969) and 50.0 mg/L for the crayfish Orconectes nais (Sanders, 1970).

Chronic toxicity studies were undertaken by Macek et al (1976) with the fathead minnow (Pimephales promelas) and the water

flea (Daphnia magna). Conclusions from these studies indicated that the safe maximum acceptable toxicant concentration (MATC) for the fathead minnow was 1.9 µg/L. Surviving adults, exposed to concentrations of 5.1 µg/L exhibited delayed spawning of approximately 100 days. Survival of Daphnia magna was reduced at trifluralin concentrations of 7.2 µg/L. Such effects were not noted at concentrations of 2.7 µg/L.

Trifluralin was found to accumulate in fish and in snails. Concentrations of 0.775 µg/g and 27.085 µg/g have been observed in fish and snails, respectively (Sanborn, 1974).

Crosby and Leitis (1973) and Leitis and Crosby (1974), reported 25 metabolites resulting from photodecomposition of the parent trifluralin material. Sanborn (1974) identified two of these, namely 2-ethyl 5-trifluoromethyl-7-nitrol-1-propylbenzimidazole and 2-ethyl-5-trifluoromethyl-7-nitrobenimidazole at concentrations of 0.04 µg/g and 0.052 µg/g in fish. Other metabolites have also been identified and quantified in fish flesh. Sanborn (1974) found the total trifluralin plus metabolites at concentrations of 1.323 µg/g and 28.870 µg/g in fish and snails, respectively. These corresponded to bioconcentration factors of 7200 and 157000, respectively, above the original ambient trifluralin water concentration.

Manitoba's proposed surface water quality objectives (Williamson, 1983) states that "concentrations of pollutants that are persistent or have accumulative effects should not exceed 0.01 of the 96 hr LC_{50}". This resulted in ambient water quality objectives ranging from 0.41 µg/L to 1.52 µg/L for rainbow trout (Salmo gairdneri) and 0.47 µg/L to 1.97 µg/L for the bluegill (Lepomis macrochirus). This tentative objective would have been lower had more sensitive test organisms been utilized. These values were, however, in agreement with the safe level of 1.9 µg/L resulting from the chronic studies of Macek et al (1976) for the fathead minnow (Pimephales promelas).

Concentrations in the La Salle and Assiniboine Rivers are, at present, below these tentative objective values.

3.3 Azinphos-methyl

Azinphos-methyl or O, O-Dimethyl S-[(4-oxo-1, 2, 3-benzotriazin-3(4H)-yl) methyl)] phosphorodithioate is the active ingredient within the insecticide Guthion. Azinphos-methyl is recommended by Manitoba Agriculture (1984a) for use in the control of a variety of insect pests on several crops. These include the diamondback moth, flea beetle, red turnip beetle, sunflower beetle, thistle caterpillar on oil seed crops, sweet clover weevil on forage crops, plus the cucumber beetle, colorado potato beetle and leaf roller on vegetable crops.

Azinphos-methyl was detected at trace levels (<0.5 µg/L) in seven samples (26%) collected from two locations on the La Salle River (Table 4). Samples containing confirmed concentrations of azinphos-methyl were collected during the period April 20, 1983 to May 2, 1983.

Frank et al (1982) reported that 2330 kg of azinphos-methyl had been utilized within 11 watersheds in southern Ontario during 1975. However, azinphos-methyl loss to surface waters draining the study area was not observed.

It was determined that azinphos-methyl was used in the vicinity of the La Salle River sampling sites in order to control flea beetles on rapeseed during 1982. While only preliminary, the results of the present investigation indicated that losses to surface water may have occurred from the application site.

La Salle River flows during the study period had diminished to between 0.198 and 0.501 m^3/s from peak discharges of 8.95 m^3/s recorded two days prior to commencement of sampling. The transport mechanism of azinphos-methyl to the La Salle River is not known, but appeared associated with surface runoff resulting from spring snow-melt.

Maximum acceptable concentrations have not been included for azinphos-methyl by Health and Welfare Canada (1978) in the document "Guidelines for Canadian Drinking Water Quality, 1978". However, the National Academy of Sciences (1977) recommended an acceptable daily intake (ADI) for azinphos-methyl of 0.0125 mg/kg/day.

Table 4: Concentrations (µg/L) of azinphos-methyl in surface waters within the study area.

	La Salle R. #1	La Salle R. #2	Assiniboine R. #3	Assiniboine R. #4	Surface Runoff #5	Surface Runoff #6	Surface Runoff #7
April 11, 1983	ND[5]	ND					
April 13, 1983	ND	ND			ND		
April 18, 1983	ND	ND					
April 20, 1983	Trace[1]	Trace					
April 25, 1983	Trace	Trace					
April 27, 1983	Trace	Trace					
May 2, 1983	ND[2]	Trace	ND[2]				
June 1, 1983						ND	ND
June 14, 1983	ND	ND	ND				
July 13, 1983	ND	ND	ND				
September 12, 1983	ND	ND	ND				
October 13, 1983	ND	ND	ND				
November 8, 1983	ND		ND	ND			
December 5, 1983	ND[3]		ND	ND			
January 5, 1984	ND		ND	ND			
February 21, 1984	ND		ND	ND			
March 26, 1984	ND[4]		ND	ND			

1. Detected by Gas Chromotography and confirmed by Mass Spectrometry. Concentrations have been quantified in some cases. However, these values may only be approximate since they are below the methods detection limits.

2. Analyses were performed on a decanted sample due to the formation of a surface layer of an apparent hydrocarbon.

3. Samples were filtered through Whatman #4 qualitative paper, prior to extraction. This filtration removed 98% of the 20-25 µm size particles.

4. Samples may have contained a large proportion of snow-melt water.

5. ND = Not Detected.

Assuming that a 70 kg person ingested 1% of the ADI through the consumption of 2.0 L of water per day, resulted in an azinphos-methyl criteria in drinking water of 4.4 µg/L. The State of New York (1978) adopted this value as a groundwater standard for the protection of such water for domestic consumption purposes. However, assuming that a 70 kg person ingested 20% of the ADI through the consumption of 2.0 L of water per day, resulted in an azinphos-methyl criteria in drinking water of 87.5 µg/L. This latter assumption is consistent with that of Health and Welfare Canada (1978) used in the derivation of maximum acceptable concentrations in water for other pesticides.

The United States Environmental Protection Agency (1976a) included a summary of the aquatic life toxicity information for azinphos-methyl. They reported that bioconcentration is low (approximately 20 times) with toxicity occurring through inhibition of the enzyme acetylcholinesterase. The United States EPA (1976a) further reported that the "safe" long term exposure for fathead minnows ranges from 0.3 µg/L to 0.5 µg/L. The United States EPA (1976a) recommended a criteria of 0.01 µg/L azinphos-methyl for the protection of freshwater aquatic life, based upon a 0.1 safety factor applied to the 96 hr LC_{50} of 0.1 µg/L for the amphipod Gammarus sp.

A criteria of 0.001 µg/L azinphos-methyl was recommended by the National Academy of Sciences/National Academy of Engineering (1973) for the protection of aquatic life and wildlife.

The Great Lakes Water Quality Board (1978) recommended a criteria of 0.005 µg/L azinphos-methyl in untreated water for the protection of aquatic life. This criteria was based upon applying a safety factor of 0.05 to the 96 hr LC_{50} of 0.1 µg/L for the amphipod Gammarus fasciatus.

The above criteria may have been exceeded during the runoff period in the La Salle River. Azinphos-methyl concentrations, while confirmed, were not quantified at levels below 0.5 µg/L.

3.4 Dicamba

Dicamba, or 2-methoxy-3, 6-dichlorobenzoic acid, is a pre-emergence selective systemic herbicide suitable for the control of annual broadleaf and grassy weeds. Dicamba is contained within the herbicide formulations Banvel, Banvel 5G, Dycleer 24, Dycleer 10P, Dyvel, Killex, Kil-mor, Target plus others. These products are recommended for the control of a variety of weed pests in wheat, oats, barley, plus in certain forage crops (Manitoba Agriculture, 1984b). Dicamba is also common in formulations developed for home and garden use.

Dicamba was detected at trace levels in 3 samples (11%) collected from two sampling sites on the La Salle River on two occasions (Table 5). Dicamba was also detected at trace levels in a single sample collected from the Assiniboine River.

The presence of dicamba in the La Salle and Assiniboine Rivers appeared to coincide with the period of snow-melt water runoff, although peak stream discharge had occured approximately three weeks previous. Dicamba was not detected for the remainder of the sampling period.

Haque and Freed (1975) reported that dicamba is slightly persistent in soils, with a half-life of 0.5 to 1.5 months. The primary degradation transformation in soil and plants is oxidation and conjugation (Haque and Freed, 1975). The National Academy of Sciences (1977) reported that dicamba persists in soil for up to 7 to 10 months and is readily leached by runoff water. Further, dicamba is reported to be chemically resistant to breakdown, although rapid losses occur in water (National Academy of Sciences, 1977).

Frank et al (1982) examined dicamba losses to surface water in an investigation within 11 watersheds in southern Ontario. The highest individual dicamba concentration quantified was 0.7 µg/L. Considering that 63 kg of dicamba had been applied, a use/loss ratio of 5.0×10^{-3} was calculated. These losses were attributed to spills, drift and direct application into surface waters. Dicamba was detected immediately after application. Frank et al (1982) reported,

Table 5: Concentrations (µg/L) of dicamba in surface waters within the study area.

	La Salle R. #1	La Salle R. #2	Assiniboine R. #3	Assiniboine R. #4	Surface Runoff #5	Surface Runoff #6	Surface Runoff #7
April 11, 1983	ND[5]	ND			ND		
April 13, 1983	ND	ND					
April 18, 1983	ND	ND					
April 20, 1983	ND	ND					
April 25, 1983	ND	ND					
April 27, 1983	ND	Trace[1]					
May 2, 1983	Trace[2]	Trace[2]	Trace[2]				
June 1, 1983						ND	ND
June 14, 1983	ND	ND	ND				
July 13, 1983	ND	ND	ND				
September 12, 1983	ND	ND	ND				
October 13, 1983	ND	ND	ND				
November 8, 1983	ND		ND	ND			
December 5, 1983	ND[3]		ND	ND			
January 5, 1984	ND		ND	ND			
February 21, 1984	ND		ND	ND			
March 26, 1984	ND[4]		ND	ND			

1. Detected by Gas Chromotography and confirmed by Mass Spectrometry. Concentrations have been quantified in some cases. However, these values may only be approximate since they are below the methods detection limits

2. Analyses were performed on a decanted sample due to the formation of a surface layer of an apparent hydrocarbon.

3. Samples were filtered through Whatman #4 qualitative paper, prior to extraction. This filtration removed 98% of the 20-25 µm size particles.

4. Samples may have contained a large proportion of snow-melt water.

5. ND = Not Detected.

however, that dicamba had been applied to non-agricultural lands, such as rights-of-way or industrial sites. Thus, patterns of dicamba loss may differ somewhat between the present investigation and those of Frank et al (1982).

Maximum concentrations acceptable for lifelong consumption have not been developed by Health and Welfare Canada (1978) for dicamba in drinking water. However, following a review of the available mammalian toxicity information, the National Academy of Sciences (1977) calculated an Acceptable Daily Intake (ADI) for dicamba of 0.00125 mg/kg/day.

Assuming that 1% of the ADI could be contributed from drinking water, and considering consumption of 2.0 L of water per day by a 70 kg person, resulted in a suggested no-adverse effect level in water of 0.44 µg/L. However, assuming that 20% of the ADI could be contributed from drinking water, and considering the consumption of 2.0 L of water per day by a 70 kg person, resulted in a suggested no-adverse effect level in water of 8.75 µg/L. The State of New York (1978) adopted the concentration of 0.44 µg/L dicamba in groundwater as a standard for the protection of such waters for domestic consumption. However, the assumption made in the latter calculation was consistent with that of Health and Welfare Canada (1978) utilized in the development of guidelines for other pesticides in drinking water.

The National Academy of Sciences/National Academy of Engineering (1973) recommended a maximum acceptable dicamba concentration of 200 µg/L for the protection of freshwater aquatic life and wildlife.

Johnson and Finley (1980) reported the dicamba 96 hr LC_{50} for rainbow trout (Salmo gairdneri) to be 28 mg/L. Other species tested included the bluegill (Lepomis macrochirus) and the water flea Daphnia magna. The results of these toxicity tests were >50 mg/L and >100 mg/L dicamba, respectively. Sanders (1970) reported the 48 hr TL_{50} dicamba toxicity results for the water flea (Daphnia magna), seed shrimp (Cypridopsis vidua), scud (Gammarus fasciatus), sowbug (Asellus brevicaudus), glass shrimp (Palaemonetes kadiakensis) and the crayfish (Orconectes nais) to be greater than 100 mg/L.

Williamson's (1983) objective for Manitoba's surface waters states that "concentrations of pollutants that are non-persistent or have non-cumulative effects should not exceed 0.05 of the 96 hr LC_{50}". This resulted in a criteria for rainbow trout (Salmo gairdneri) of 1.4 mg/L dicamba. This tentative objective would have been lower had more sensitive test organisms been utilized.

It appeared, that at the present concentrations in the La Salle and Assiniboine Rivers, dicamba should not pose a threat to aquatic life. Concentrations may have approached or exceeded those levels utilized by the State of New York (1978) for the protection of drinking water supplies.

3.5 MCPA

MCPA, namely 4-chloro-2-methyl phenoxyacetic acid, is a selective, translocated, postemergence herbicide. MCPA is formulated in a variety of herbicides including Blagal, Brominal M, Buctril M, Estemine MCPA, MCPA, Stampede CM, Target, plus others. These formulations are used for the control of numerous broadleaf weed pests in forage, field crops and in home and garden situations.

MCPA was detected in 22% of the samples collected from two sites on 27 occasions from the La Salle River. Additionally, two out of 15 samples collected from two sites on the Assiniboine River contained traces of MCPA at 0.1 µg/L and 0.02 µg/L. MCPA concentrations in the La Salle River, although less than the specific methods detection limits, were approximately quantified to range from trace (<0.5 µg/L) to 0.3 µg/L. A pattern of contamination of the La Salle and Assiniboine Rivers was not apparent.

Frank et al (1982) investigated pesticides in runoff water from 11 watersheds in Ontario and reported MCPA being detected in 0.9% of the samples collected during 1975/1976. The maximum MCPA concentration detected was 0.3 µg/L. MCPA loss to surface water was attributed to spills, drift and direct application. Levels of MCPA were rapidly reduced to non-detectable concentrations. Considering that 697 kg of MCPA had been used within the study area, Frank et al (1982) calculated a use/loss ratio of 4.6×10^{-4}.

Table 6: Concentrations (µg/L) of MCPA in surface waters within the study area.

	La Salle R. #1	La Salle R. #2	Assiniboine R. #3	Assiniboine R. #4	Surface Runoff #5	Surface Runoff #6	Surface Runoff #7
April 11, 1983	ND[5]	ND			ND		
April 13, 1983	ND	ND					
April 18, 1983	Trace (0.09)	ND					
April 20, 1983	ND	ND					
April 25, 1983	ND	ND					
April 27, 1983	ND	Trace[1]					
May 2, 1983	ND[2]	ND[2]	Trace(0.1)[2]				
June 1, 1983						ND	ND
June 14, 1983	ND	Trace	ND				
July 13, 1983	ND	ND	ND				
September 12, 1983	Trace (0.3)	Trace (0.1)	ND				
October 13, 1983	ND	Trace (0.1)	Trace (0.02)				
November 8, 1983	ND		ND	ND			
December 5, 1983	ND[3]		ND	ND			
January 5, 1984	ND		ND	ND			
February 21, 1984	ND		ND	ND			
March 26, 1984	ND[4]		ND	ND			

1. Detected by Gas Chromotography and confirmed by Mass Spectrometry. Concentrations have been quantified in some cases. However, these values may only be approximate since they are below the methods detection limits.

2. Analyses were performed on a decanted sample due to the formation of a surface layer of an apparent hydrocarbon.

3. Samples were filtered through Whatman #4 qualitative paper, prior to extraction. This filtration removed 98% of the 20-25 µm size particles.

4. Samples may have contained a large proportion of snow-melt water.

5. ND = Not Detected.

Haque and Freed (1975) reported that MCPA is slightly persistent in soils, with a half-life of 0.5 to 1.5 months.

The National Academy of Sciences (1977) recommended an acceptable daily intake (ADI) for MCPA of 0.00125 mg/kg/day. Assuming that 1% of this ADI could be derived from drinking water and assuming that 2.0 L of water could be consumed daily by a 70 kg person, resulted in a suggested no-adverse-effect level for drinking water of 0.44 µg/L. The State of New York (1978) promulgated this value as a groundwater standard for the protection of drinking water supplies. However, assuming that 20% of the ADI could be ingested from drinking water by a 70 kg person consuming 2.0 L of water per day, resulted in a suggested no-adverse-effect level of 8.75 µg/L. This latter assumption is consistent with that of Health and Welfare Canada (1978) used for the development of guidelines for other pesticides in drinking water.

The National Research Council of Canada (1978) reported that the phenoxy herbicides do not accumulate in the aqueous environment in the same manner as do the chlorinated organics. They further reported that a significant fraction of the MCPA load is entrained by aquatic plants, such as algae, and emergent and submergent macrophytes. Residues in aquatic plant tissues were observed to persist for up to 2 - 6 months. They further reported that bioconcentration did not appear to be significant in organisms other than zooplankton and aquatic plants.

Limited aquatic animal toxicity tests have been conducted with MCPA. However, the National Research Council of Canada (1978) reported the 24 hr LC_{50} and 48 hr LC_{50} for the bluegill (Lepomis macrochirus) to be 164 mg/L. They further reported the 48 hr LC_{50} for the perch (Perca flavescens) and guppy to range from 200 mg/L to 215 mg/L and 30 mg/L to 40 mg/L, respectively.

Williamson's (1983) objective states that "concentrations of pollutants that are non-persistent or have non-cumulative effects should not exceed 0.05 of the 96 hr LC_{50}". This resulted in a MCPA

criteria ranging from near 1.5 mg/L to 10.75 mg/L. This tentative objective would have been lower had more sensitive test organisms been utilized.

Based upon the limited information available, it appeared that the present concentrations of MCPA in the La Salle and Assiniboine Rivers do not pose a threat to aquatic life. Ambient concentrations of MCPA did not exceed the available criteria derived for the protection of human health following long-term consumption. However, concentrations approached those adopted by the State of New York for the protection of groundwaters suitable for drinking purposes.

3.6 Diclofop-methyl

Diclofop-methyl or methyl 2-[4-(2',4'-dichlorophenoxy)-phenoxy] propanoate, is the active ingredient within the herbicide Hoegrass. Hoegrass is both a contact and systemic postemergence foliar herbicide used for the control of grassy weeds (Manitoba Agriculture, 1984b).

Diclofop-methyl was detected in 14 out of 27 samples (52%) collected from the La Salle River at two sampling sites. Concentrations ranged from trace (<0.5 µg/L) to 4.0 µg/L. A pattern of contamination was not evident. However, diclofop-methyl residues appeared to persist at trace levels throughout most of the ice-free season.

Diclofop-methyl was not detected in samples collected from the Assiniboine River.

Scientific information is too limited to assess the human health significance of the concentrations of diclofop-methyl detected in the La Salle River.

Information is sparse on the environmental fate and transport of diclofop-methyl. It is, however, thought to be similar to other phenoxy herbicides.

Table 7: Concentrations (µg/L) of diclofop-methyl in surface waters within the study area.

	La Salle R. #1	La Salle R. #2	Assiniboine R. #3	Assiniboine R. #4	Surface Runoff #5	Surface Runoff #6	Surface Runoff #7
April 11, 1983	Trace [1]	Trace			ND		
April 13, 1983	Trace	Trace					
April 18, 1983	Trace (0.08)	Trace					
April 20, 1983	4.0	Trace (0.08)					
April 25, 1983	ND[5]	ND					
April 27, 1983	ND	ND					
May 2, 1983	ND[2]	ND[2]	ND[2]				
June 1, 1983						ND	ND
June 14, 1983	ND	Trace	ND				
July 13, 1983	Trace (0.1)	Trace (0.2)	ND				
September 12, 1983	Trace	Trace	ND				
October 13, 1983	Trace (0.03)	ND	ND				
November 8, 1983	Trace		ND	ND			
December 5, 1983	ND[3]		ND	ND			
January 5, 1984	ND		ND	ND			
February 21, 1984	ND		ND	ND			
March 26, 1984	ND[4]		ND	ND			

1. Detected by Gas Chromotography and confirmed by Mass Spectrometry. Concentrations have been quantified in some cases. However, these values may only be approximate since they are below the methods detection limits.

2. Analyses were performed on a decanted sample due to the formation of a surface layer of an apparent hydrocarbon.

3. Samples were filtered through Whatman #4 qualitative paper, prior to extraction. This filtration removed 98% of the 20-25 µm size particles.

4. Samples may have contained a large proportion of snow-melt water.

5. ND = Not Detected.

The acute oral LD_{50} for the rat is reported to be 679 mg/kg (Farm Chemicals, 1982). Johnson and Finley (1980) reported the 96 hr LC_{50} of diclofop-methyl to rainbow trout (Salmo gairdneri) and bluegill (Lepomis macrochirus) to be 0.25 mg/L and 0.54 mg/L, respectively. Diclofop-methyl appeared to be one of the most toxic toward aquatic animals in comparison to other phenoxy herbicides examined by Johnson and Finley (1980) and by the National Research Council of Canada (1978).

Although the aquatic toxicity data base is limited to tests on only two animals, tentative criteria were developed using the objective of Williamson (1983). This objective states that "concentrations of pollutants that are non-persistent or have non-cumulative effects should not exceed 0.05 of the 96 hr LC_{50}". This resulted in diclofop-methyl criteria for the protection of aquatic life ranging from 12.5 µg/L to 27.0 µg/L for the rainbow trout (Salmo gairdneri) and bluegill (Lepomis macrochirus), respectively. These criteria would have been lower, had chronic and acute toxicity tests been conducted on more sensitive organisms. Maximum diclofop-methyl concentrations in the La Salle River were below these tentative criteria.

3.7 2,4-D

2,4-D, or 2,4-dichlorophenoxy acetic acid, is the active ingredient in numerous herbicide formulations used for the postemergence foliar control of broadleafed plants. 2,4-D was detected in 23 out of 33 samples (70%) collected at two sites from the La Salle River. Concentrations ranged from 0.011 µg/L to 0.130 µg/L, with mean 2,4-D levels of <0.055 µg/L. 2,4-D concentrations appeared to persist throughout April, May and June of 1983. This corresponded with the period of spring melt-water runoff and with the normal period of agricultural application. Residues were also detected in September, 1983, and in samples collected under ice cover in March, 1984. Spring melt water runoff had begun at the time of sample collection in March, 1984. 2,4-D was not detected in samples collected from the Assiniboine River. However, 2,4-D was detected and

Table 8: Concentrations (µg/L) of 2,4-D in surface waters within the study area.

	La Salle R. #1	La Salle R. #2	Assiniboine R. #3	Assiniboine R. #4	Surface Runoff #5	Surface Runoff #6	Surface Runoff #7
April 11, 1983	0.073	0.064			ND		
April 13, 1983	0.074	0.049					
April 15, 1983	0.097	0.089			0.058		
April 18, 1983	0.092	0.121					
April 20, 1983	0.100	0.130					
April 22, 1983	0.114	0.114					
April 25, 1983	0.032	0.035					
April 27, 1983	0.036	0.054					
April 29, 1983	0.054	0.112					
May 2, 1983	ND[2]	0.104					
June 1, 1983						ND	ND
June 14, 1983	0.024	0.013	ND				
July 13, 1983	ND	ND	ND				
September 12, 1983	ND	0.011	ND				
October 13, 1983	ND	ND	ND				
November 8, 1983	ND		ND	ND			
December 5, 1983	ND		ND	ND			
January 5, 1984	ND		ND	ND			
February 21, 1984	ND		ND	ND			
March 26, 1984	0.12[1]		ND	ND			

1. Samples may have contained a large proportion of snow-melt water.

2. ND = Not Detected.

quantified at 0.058 µg/L in a single sample collected from ponded surface water in the study area. These levels appeared consistent with 2,4-D concentrations quantified in other streams in Manitoba, such as the Red and Souris Rivers at Emerson and Coulter, respectively (Environment Canada, 1980 and 1982).

The time required for the disappearance of 50% of the applied 2,4-D in soil is usually several days (National Research Council of Canada, 1978). Microbial degradation appeared to be the causative agent for most 2,4-D decomposition.

Frank et al (1982) investigated the presence of agricultural pesticides in surface runoff water in 11 watersheds in Ontario. 2,4-D was detected in 8.1% and 5.8% of the samples collected in 1975/1976 and 1976/1977, respectively. The highest individual concentration was 320 µg/L. The mean concentrations for 1975/1976 and 1976/1977 were 0.7 µg/L and <0.1 µg/L, respectively. Frank et al (1982) computed a use/loss ratio of 1.5×10^{-3}, given that 3098 kg of 2,4-D was used in the study area during the investigation. Frank et al (1982) attributed the majority of 2,4-D losses to surface water to spills, drift and direct application to watercourses. However, storm runoff, including snow-melt events were also considered a factor, along with 2,4-D application to non-agricultural lands such as roadways and ditches.

The pattern of 2,4-D loss reported by Frank et al (1982) appeared similar to that observed during the present investigation.

Health and Welfare Canada (1978) recommended a maximum 2,4-D concentration acceptable for lifelong consumption in drinking water of 0.1 mg/L. This was determined from an acceptable daily intake (ADI) of 0.016 mg/kg/day (United States Environmental Protection Agency, 1976b), assuming that a 70 kg person consumed 20% of this ADI through the ingestion of 2.0 L of water per day.

The 2,4-D concentrations in the La Salle River were considerably lower than the maximum acceptable concentrations recommended by Health and Welfare Canada (1978).

The National Research Council of Canada (1978) provided a detailed examination of the transport and fate of chlorophenoxy herbicides in the environment, with the majority of the information on 2,4-D.

2,4-D can be formulated in herbicides as various acids, esters and salts, each with unique toxicological characteristics. The National Research Council of Canada (1978) reported that some esters have 24 hr LC_{50} and 48 hr LC_{50} values for fish of less than 1 mg/L. However, rapid hydrolosis to the less toxic acid forms usually reduces the toxic effects. They reported, however, that secondary effects on the aquatic ecosystem may be more significant than direct toxic effects. Secondary effects include the destruction of plant communities with the inherent effects on reduced cover offered benthic communities, increased nutrient release and reduced photo-respiration.

Williamson's (1983) objectives states that "concentrations of pollutants that are non-persistent or have non-cumulative effects should not exceed 0.05 of the 96 hr LC_{50}". This resulted in an approximate tentative objective for the most apparent toxic 2,4-D derivative of 50 µg/L. This objective would have been lower had more sensitive aquatic species been tested.

The National Research Council of Canada (1978) however, reported that the long term exposure to low 2,4-D concentrations has not been intensively studied. Where field studies have been undertaken, they have usually been conducted in the southern United States. Extrapolation to the cooler climate of Manitoba may not be appropriate since degradation may occur at a much reduced rate.

4. Conclusions

Water samples were collected from the La Salle and Assiniboine Rivers during 1983/1984 and were analyzed for twenty-seven agricultural pesticides. The herbicides triallate, trifluralin, dicamba, MCPA, diclofop-methyl and 2,4-D plus the insecticide azinphos-methyl were detected in samples collected from the La Salle River. The herbicides triallate, trifluralin, dicamba and MCPA were detected in samples collected from the Assiniboine River.

The mechanism of transport from the application site to these streams was not a part of this study but appeared related to snow melt and rainfall runoff events. The results and associated water quality criteria are summarized in Table 9.

It was concluded that:

(a) scientific literature was too limited to assess the human health significance of the triallate concentrations detected in the La Salle and Assiniboine Rivers. Furthermore, literature was insufficient to determine the significance of the observed triallate concentrations towards aquatic life in the La Salle and Assiniboine Rivers.

(b) ambient concentrations of trifluralin did not exceed the available criteria derived for the protection of human health following long-term consumption. Further investigations are required to assess the significance of the reported carcinogenic response exhibited by trifluralin towards one laboratory animal species tested. Trifluralin concentrations did not exceed tentative water quality objectives suitable for the long-term protection of aquatic life calculated from acute and chronic toxicity tests.

(c) ambient concentrations of azinphos-methyl in the La Salle and Assiniboine Rivers did not exceed the available criteria derived for the protection of human health. However, it appeared probable that azinphos-methyl concentrations exceeded tentative water quality objectives suitable for the long-term protection of aquatic life that were calculated from acute toxicity tests.

(d) ambient concentrations of dicamba in the La Salle and Assiniboine Rivers did not exceed the available criteria derived for the protection of human health. Dicamba, at the detected concentrations, should not pose a threat to the long-term safety of aquatic life.

(e) ambient concentrations of MCPA in the La Salle and Assiniboine Rivers did not exceed the available criteria derived for the protection of human health. MCPA concentrations did not exceed calculated tentative water quality objectives suitable for the long-term protection of aquatic life.

(f) scientific information is too limited to determine the human health significance of the concentrations of diclofop-methyl in the La Salle River. Diclofop-methyl concentrations did not exceed calculated tentative water quality objectives suitable for the long-term protection of aquatic life.

(g) ambient concentrations of 2,4-D in the La Salle River did not exceed the available criteria derived for the protection of human health. Observed 2,4-D concentrations should not pose a long-term threat to the aquatic life in the La Salle River.

Table 9: Summary of the pesticide results, with available criteria for the protection of drinking water and criteria for the protection of aquatic life.

	Results (range) µg/L		Criteria for the Protection of Drinking Water (µg/L)					Criteria for the Protection of Aquatic Life (µg/L)				
Pesticides	La Salle River	Assiniboine River	1	2	3	4	5	6	7	8	9	10
triallate	trace(<0.05)-0.15	trace(<0.05)-trace (0.01)										
trifluralin	trace(<0.05)-0.24	trace(<0.05)-trace	700.0	35.0		70.0	3.5				0.41	1.9
azinphos-methyl	trace(<0.5)		87.5	4.4				0.01	0.005	0.001		
dicamba	trace(<0.5)	trace(<0.05)	8.75	0.44						200.	1400	
MCPA	trace(<0.5)-trace (0.3)	trace(0.02)-trace (0.1)	8.75	0.44							1500	
diclofop-methyl	trace(<0.5)-4.0										12.5	
2,4-D	0.011 - 0.130		87.5	4.4	100						50	

References and Notes

1. National Academy of Sciences (1977). Assumptions: Average weight of human adult = 70 kg. Average daily intake of water = 2 L; 20% of ADI assignment to water; 80% from other sources.
2. National Academy of Sciences (1977). Assumptions: Average weight of human adult = 70 kg. Average daily intake of water = 2 L; 1% of ADI assignment to water; 99% from other sources.
3. Health and Welfare Canada (1978).
4. Toft (1984). pers. comm. Calculated from the ADI of 0.01 mg/kg/day utilized by Health and Welfare Canada for deriving Division 15, Federal Food and Drug Regulations for maximum residue limits on carrots. Assumptions: (same as in 1 above).
5. Toft (1984). pers. comm. Calculated from the ADI of 0.01 mg/kg/day utilized by Health and Welfare Canada for deriving Division 15, Federal Food and Drug Regulations for maximum residue limits on carrots. Assumptions: (same as in 2 above).
6. United States Environmental Protection Agency (1976a).
7. Great Lakes Water Quality Board (1978).
8. National Academy of Sciences/National Academy Engineering (1973).
9. Williamson (1983). Calculated from methods proposed in Volume 1: Surface Water Quality Objectives of the Surface Water Quality Management Proposal documents.
10. Macek et al (1976).

5. References

Braun, H. E., and R. Frank. 1980. Organochlorine and organophosphorus insecticides, their use in eleven agricultural watersheds and their loss to stream waters in southern Ontario, Canada, 1975-1977. Sci. Total Environ. 15:169-192.

Crosby, D. G., and E. Leitis. 1973. The photodecomposition of trifluralin in water. Bull. Environ. Contam. Toxicol., 10(4):237-241.

Environment Canada. 1980. Detailed Surface Water Quality Data, Manitoba, 1974-1976. Inland Waters Directorate, Western and Northern Region, Water Quality Branch, Winnipeg, Manitoba.

Environment Canada. 1982. Detailed Surface Water Quality Data, Manitoba, 1977-1979. Inland Waters Directorate, Western and Northern Region, Water Quality Branch, Winnipeg, Manitoba.

Farm Chemicals. 1982. Farm Chemicals Handbook 1982. Melster Publishing Co. Willoughby, Ohio, 44094.

Fedoruk, A. N. 1970. Proposed Watershed Divisions of Manitoba. Manitoba Department of Mines and Natural Resources, Canada Land Inventory. Report No. 10. Winnipeg.

Frank, R., K. Montgomery, H. E. Braun, A. H. Berst, and K. Lotus. 1974. DDT and dieldrin in watersheds draining the tobacco belt of southern Ontario. Pestic. Monit. J. 8:184-201.

Frank R., and G. J. Sirons. 1979. Atrazine: its use in corn production and its loss to stream water in southern Ontario. 1975-77. Sci. Total Environ. 12:223-239.

Frank R., and G. J. Sirons. 1980. Chlorophenoxy and chlorobenzoic acid herbicides; their use in eleven agricultural watersheds and their loss to stream waters in southern Ontario, Canada, 1975-77. Sci. Total Environ. 15:149-167.

Frank, R., H. E. Braun, and M. V. H. Holdriner. 1981. Residues from past uses of organochlorine insecticides and PCB in water draining eleven agricultural watersheds in southern Ontario, Canada. 1975-1977. Sci. Total Environ. 20:255-276.

Frank, R., H. E. Braun, M. Van Hove Holdrinet, G. J. Sirons, and B. D. Ripley. 1982. Agriculture and water quality in the Canadian Great Lakes Basin: V. Pesticide use in 11 agricultural watersheds and presence in stream water, 1975-1977. J. Environ. Qual. 11:497-505.

Great Lakes Water Quality Board. 1978. Group 2, New and Revised Specific Water Quality Objectives Proposed for the 1972 Agreement Between the United States and Canada on Great Lakes Water Quality. International Joint Commission. Windsor, Ontario.

Griesemer, R. A., and C. Cueto, Jr. 1980. Toward a classification scheme for degrees of experimental evidence for carcinogenicity of chemicals for animals. Molecular and Cellular Aspects of Carcinogen Screening Tests. International Agency for Research on Cancer/World Health Organization/Commission of the European Communities/Directorate General for Research, Science and Education. Lyon, 1980. pp. 259-281.

Haque, R. and V. H. Freed. 1975. Environmental Dynamics of Pesticides. Plenum Press, New York and London. pp. 837.

Health and Welfare Canada. 1978. Guidelines for Canadian Drinking Water Quality. Federal-Provincial Working Group on Drinking Water of the Federal-Provincial Advisory Committee on Environmental and Occupational Health. Ottawa, Ontario. pp. 76.

Johnson, W. W., and M. T. Finley. 1980. Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates. U. S. Dept. of the Interior, Fish and Wildlife Service. Resource Publication 137. Washington, D.C. 1980.

Leitis, E., and D. G. Crosby. 1974. Photodecomposition of trifluralin. J. Agr. Food Chem., 22(5):842-848.

Macek, K. J., C. Hutchinson, and O. B. Cope. 1969. The effects of temperature on the susceptibility of bluegills and rainbow trout to selected pesticides. Bull. Environ. Contam. Toxicol., 4(3):174-183.

Macek, K. J., M. A. Lindberg, S. Sauter, K. S. Buxton, and P. A. Costa. 1976. Toxicity of four pesticides to water fleas and fathead minnows. Acute and chronic toxicity of acrolein, heptachlor, endosulfan, and trifluralin to the water flea (Daphnia magna) and the fathead minnow (Pimephales promelas). U. S. Environmental Protection Agency, Ecological Research Series EPA-600/3-76-099. Washington, D.C. ix + 58 p.

Manitoba Agriculture. 1984a. Manitoba Insect Control Guide. Manitoba Department of Agriculture. Winnipeg. pp. 47.

Manitoba Agriculture. 1984b. Guide to Chemical Weed Control. Manitoba Department of Agriculture. Agdex 641. Winnipeg. pp. 113.

Menzie, C. M. 1974. Metabolism of Pesticides - An Update. United States Department of the Interior, Fish and Wildlife Service. Special Scientific Report - Wildlife No. 184. Washington, D. C. pp. 485.

Miles, R. J. W., and C. F. Harris. 1971. Insecticide residues in a stream and a controlled drainage system in agricultural areas of southwestern Ontario. 1970. Pestic. Monit. J. 5:289-294.

Miles, J. R. W., and C. R. Harris. 1973. Organochlorine insecticide residues in streams draining agricultural, urban and resort areas of Ontario, Canada. 1971. Pestic. Monit. J. 6:363-368.

Mowchenko, P., P. O. Meid. 1983. The determination of gross and effective drainage areas in the prairie provinces. Hydrology report #104. Engineering Branch, Prairie Farm Rehabilitation Administration, Agriculture Canada. Regina, Saskatchewan.

Nash, R. G. 1983. Comparative volatilization and dissipation rates of several pesticides from soil. J. Agric. Food Chem. 1983. 31:210-217.

National Academy of Sciences/National Academy of Engineering. 1973. Water Quality Criteria, 1972. EPA. R3.73.033. March 1973. Washington, D.C. 594 pages.

National Academy of Sciences. 1977. Drinking Water and Health. Safe Drinking Water Committee, Advisory Center on Toxicology, Assembly of Life Sciences, National Research Council. Washington, D.C. pp. 939.

National Research Council of Canada. 1978. Phenoxy Herbicides - Their Effects on Environmental Quality with Accompanying Scientific Criteria For 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD). Publication No. NRCC 16075 of the Environmental Secretariat. Ottawa.

O'Brien, R. P. and J. L. Fisher. 1983. There is an answer to groundwater contamination. Water/Engineering and Management, May 1983.

Roberts, G. G., G. J. Sirons, R. Frank, and H. E. Collins. 1979. Triazine residues in a watershed in southwestern Ontario. J. Great Lakes Res. 5:246-255.

Sanborn, J. R. 1974. The Fate of Select Pesticides in the Aquatic Environment. U. S. Environmental Protection Agency. EPA - 660/3-74-025.

Sanders, H. O. 1969. Toxicity of pesticides to the crustacean Gammarus lacustris. U. S. Bur. Sport Fish. Wildl. Tech. Pap. 25. 18p.

Sanders, H. O. 1970. Toxicities of some herbicides to six species of freshwater crustaceans. Water Pollution Control Federation Journal 42(8) Part 1:1544-1550.

State of New York. 1978. Groundwater Classifications, Quality Standards and Effluent Standards and/or Limitations. Title 6, Official Compilation of Codes, Rules and Regulations, Part 703. New York State Department of Environmental Conservation. September, 1978. New York.

United States Environmental Protection Agency. 1976(a). Quality Criteria for Water. Washington, D. C., 20460.

United States Environmental Protection Agency. 1976(b). National Interim Primary Drinking Water Regulations. U. S. Government Printing Office, Washington, D. C.

Water Survey of Canada. 1983. Historical Streamflow Summary: Manitoba to 1982. Inland Waters Directorate, Water Survey of Canada. Ottawa.

Williamson, D. A. 1982. A conductivity study on the La Salle River, 1980 - 1981. Water Standards and Studies Report #82-18. Environmental Management Division. Winnipeg.

Williamson, D. A. 1983. Surface Water Quality Management Proposal. Volume 1: Surface Water Quality Objectives. Water Standards and Studies Report #83-2. Department of Environment and Workplace Safety and Health. Winnipeg.

Zaki, M. H., D. Moran and D. Harris. 1982. Pesticides in groundwater: the aldicarb story in Suffolk County, NY. American Journal of Public Health 72(12):1391-1395.

6. Acknowledgements

I gratefully acknowledge the provisions of funds for analyses of the pesticides triallate, trifluralin, azinphos-methyl, dicamba, MCPA, bromoxynil and diclofop-methyl under terms of the Canada, Manitoba Agreement on Water Development for Regional Economic Expansion and Drought Proofing. I also thank the staff of the Department of Natural Resources, Water Resources Branch, Hydrotechnical Services Branch for conducting the survey of landowners in the Elie area and for collecting the initial water samples.